Semiconductor-Metal Graded Index Composite Thin Films for Infrared Applications

by

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ABSTRACT

Theoretical /experimental studies have been carried out on Germanium:Silver (Ge:Ag) graded index composite thin films, which demonstrate that graded coatings, consisting of varied concentrations of Ag with respect to the Ge film thickness, exhibit different optical properties ranging from selective infrared (IR) reflectance to broad-band IR absorptance. The graded coatings have been produced by dc magnetron co-sputtering of Ge and Ag and the spectral properties are found to be stable against temperature. The coatings have been applied to a novel infrared tunnel sensor (micro-Golay cell) to improve the device performance.

Key words: Inhomogeneous, Graded Index, Composite Films, Germanium, Silver, Infrared Tunnel Sensor, Thermal Emissivity.

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1. Introduction:

Composite optical thin films are unique among the family of optical thin films in that optical properties not realizable within the scope of conventional materials can be obtained. The composite thin films can be either optically homogeneous or inhomogeneous and the constituent materials are generally any one of the following: dielectric-dielectric,[1,2] dielectric-metal[3-5] and semiconductor-metal.[6] The theoretical and experimental studies carried out on the inhomogeneous dielectric-dielectric combination have shown that graded index dielectric films can be produced by combining suitable optical materials and the films can be used to develop rugate filters and wideband antireflection coatings.[7,8] Similarly, graded index insulator-metal (Cermet structures) coatings are excellent solar absorbers[5,9-11]. Further studies are being carried out to explore more interesting applications of these categories of films.[12,13] However, there are few studies which either illustrate or demonstrate the application of semiconductor-metal composite thin films. In view of this, systematic studies have been carried out on the preparation and characterization of semiconductor-metal composite thin films. The initial investigation focussed on optically homogeneous composite films of Ge:Ag. It has been shown that the films can be prepared by dc magnetron co-sputtering and they exhibit a wide range of optical properties, from medium reflection/low absorption to high reflection/absorption which can be controlled by the metallic content in the composite film[6].

In this paper we have extended the investigation to inhomogeneous thin films with particular reference to the optical properties of graded index films. After discussing the theoretical model calculations on graded index composite films, we present the experimental results, highlighting the optical properties of the films, the thermal stability of the optical properties, and the application of the films to specific opto-electronic systems.

2. Theoretical Analysis:

A semiconductor-metal thin film, such as Ge:Ag can be structured by grading the metallic concentration with respect to the thickness of the Ge film. The grading can be linear or quadratic Ideally the metallic concentration can be increased or decreased monotonically with respect to the thickness. However, we have considered grading profiles, approximating the linear and quadratic forms, in which the metallic concentration is decreased from a specific value in discontinuous steps, as illustrated in Fig. 1. These profile forms are chosen due to their easy accessibility for experimental reproduction, as will be shown later. The variations of the optical function, $f = (n^2 + k^2)^{1/2}$ with respect to the film thickness, for the different grading profiles, are shown in Fig. 2. The results indicate that the gradation of the optical function is steeper than the gradation of the metallic concentration. This occurs because the optical constants of Ge:Ag composite films vary non-linearly with respect to the metallic concentration.[6]

In the present theoretical calculations, the graded structure is considered to be deposited on an opaque silver coating whose optical constants are obtained from a Drude equation,[14]

$$\epsilon = -\frac{\omega_p^2}{\omega(\omega + i\omega_\tau)} \qquad (1)$$

where ω_p is the plasma frequency, ω_τ is the inverse relaxation time, and ω is the frequency of the infrared radiation. ω_p and ω_τ are set equal to those of Ag.[6,14] The optical constants (i.e. the refractive index, n, and the absorption index, k) of the Ge:Ag composite layers constituting the graded structure are calculated from the polynomial equation[6],

$$\begin{pmatrix} n \\ k \end{pmatrix} = \sum_1^5 \begin{pmatrix} P_m \\ Q_m \end{pmatrix} F^{m-1} \qquad (2)$$

where F is the volume fraction/concentration of Ag, and P_m and Q_m are the polynomial coefficients which have been determined by detailed experimental/theoretical studies of homogeneous Ge:Ag composite thin films[6].

As can be seen from Figs. 1 and 2, the present graded structures can be simplified to a stack of homogeneous films each with definite optical constants, n and k, and thickness d. Thus the reflectance of the graded film has been calculated using the matrix method given in Born and Wolf.’* The calculated reflectance characteristics, for 0.5 and 1.0 μm thickness films, are shown in Figs. 3a and 3b respectively. It follows from these figures that the coatings have low reflectance in the near infrared (NIR) and middle infrared regions (MIR), and high reflectance in the far infrared region (FIR). Thus, the semiconductor-metal graded coatings can be efficient absorbers in the NIR and MIR regions, and high reflectors in the FIR. As will be shown later from experimental studies and confirmed by theoretical calculations, these are the inherent properties of the graded films, irrespective of the nature of the substrate, in the region of coating thickness under investigation. However, a Ag coating beneath the graded structure is essential to maintain high reflectance characteristics beyond 400 cm-' in the region of which the optical interference effects are negligible.

It is important to add that the effect of addition of metal to a transparent semiconducting layer deposited on a highly reflecting layer is significant. This minimizes the reflection oscillations and enhances the absorption. These effects are non-linear with respect to the thickness of the coating, as can be seen from the results in Figs 3a and 3b. This is mainly due to the non-linear characteristics of the optical constants n and k with respect to the wavenumber and volume fraction of metal the typical results of which are shown in Figs 2a and 2b. It can also be seen from Figs 3a and 3b that the linearly graded film has more reflectance variation than the other. The reason is that the linearly graded film has lower absorption because of lesser metal content, resulting in more variation in reflectance with 'respect to the wavenumber. The increase in thickness of the coating enhances the absorption region, because of increased optical density (higher k), which is also obvious results shown in Figs 3a and 3b. Considering these theoretical observations and their impact on system applications, experiments were conducted to fabricate similar coating structures and study their optical properties.

3. Experimental

The experimental set-up and the conditions for preparation of the graded coatings are identical to those used for preparation of the homogeneous thin films of Ge:Ag.[6] The dc co-sputtering process, adapted for preparation of the coatings, is programmed to keep the sputtering rate of Ge constant and vary the sputtering rate of Ag to give the required concentration/volume fraction. Typical input current characteristics maintained for deposition of a 0.5 μm linearly graded coating are shown in Fig. 4. The coatings are deposited on optically polished and cleaned Zinc Selenide substrates, Ag coated soda lime glass substrates, and thin soda lime glass cover slips. The films sputtered on thin soda lime glass microslide cover slips are used for stress pattern observations. It may be noted that in all the films, a neutral stress state has been achieved, indicating that the films are mechanically very stable.

The infrared reflectance of the samples are characterized using a Laser Analytic FTIR spectrophotometer, Model No. FX-40, over the spectral range from 4000 to 400 cm^{-1} and the UV-Visible-NIR spectra are characterized using a Cary spectrophotometer, Model No. 5E, over the wavelength range from 200 to 2500 nm. The in-situ high temperature spectral reflectance are also measured using the FTIR spectrophotometer for which the sample cell is heated by means of MINCO microfoil heaters and the temperature measured using a chromel-alumel thermocouple to an accuracy of ±0.1°C. The spectral reflectance of a sample is normalized against the reflectance of a freshly deposited Ag coating. The measured reflectance are accurate to within ±0.005.

4. Results and Discussion:

In Fig. 5, the reflectance spectra of different Ge:Ag composite films deposited on Ag mirrors are shown and compared with the theoretical results. The layer parameters, namely geometrical thickness and volume fraction of Ag, have been adjusted to yield a minimum Root Mean Square deviation (RMSD) of (R_{Th} - R_{Expt}) [R_{Th} is the theoretical reflectance and R_{Expt} the corresponding experimental value] , and obtain a better fit to the experimental values.

In the results shown in Fig. 5a for a 0.5 μm linearly graded Ge:Ag composite film, the experimental and theoretical results have been matched within an RMSD of 0.07. Similarly, for a quadratically graded coating with a thickness of 0.5 μm and linearly graded coating of 1.0 μm thickness, the two sets of results have been matched with an RMSD of 0.05. These results are shown in Figs. 5b and 5c respectively. The discrepancy between theory and experiment is mainly due to uncertainty in fixing the grading profile of the coating, which in turn is attributed to uncertainty in the metallic concentration profile with respect to thickness, and inherent errors in the optical constants derived from the polynomial equations. It may be pointed out that in spite of all these possible uncertainties, the deviation between the theory and experiment has been less than 0.07.

Except for this difference, the experimental features are in agreement with the theoretical prediction in each of the three types of coatings. In view of the successful reproduction of the coatings and their corresponding optical properties, it is worthwhile to critically examine their optical properties from the point of view of potential applications. Since the moderately thin coatings (thickness $\approx 0.5\ \mu m$) deposited on a Ag mirror has high reflectance at far infrared regions ($R \geq 95\%$ at $v \leq 200\ cm^{-1}$) and low reflectance and high absorption ($\alpha \geq 65\%$) in the near and middle IR regions ($v \geq 700\ cm^{-1}$), they can find applications as selective reflectors in far infrared telescope optical systems. By applying a matching antireflection coating such as ZnS, the near and middle infrared reflectance can be further minimized. These selective reflector characteristics provide infrared telescope optical systems not only high throughput radiation for the desired in-band region, but also minimizes the unwanted heat radiation reaching the detector, without any additional optics.

Moderately thicker coatings (nominal thickness $\approx 1.0\ \mu m$) expand the low reflectance and high absorption ($\alpha \geq 60\%$) over a broader range (400 - 4000 cm^{-1}),[11] as can be seen from the results shown in Fig 5c. They are, therefore, very useful as broadband infrared absorbers in thermal detectors such as pyroelectrics, thermopiles and thermistor bolometers.

In Fig. 6, the optical reflectance of linearly graded coatings (coating thicknesses ≈ 0.5 μm) deposited on a Ag mirror and a ZnSe substrate are compared. They exhibit only a marginal difference from each other. From this, it can be inferred that the most of the interesting optical properties of graded coatings observed on opaque substrates, such as a Ag mirror, can be achieved on transparent IR substrates also. It is therefore possible that the graded composite films of Ge:Ag deposited on infrared transparent substrates such as mylar and kapton can allow high infrared absorption. Such coated plastic films can be used for thermal control applications in cryogenic and space born systems and the films offer an added advantage in that the thermal control coatings of different infrared emissivities can be easily produced by altering the metal content, as is obvious from the results shown in Figs. 5a - 5c.

From the point of view of thermal control applications, knowledge of the optical properties in the visible and near IR (VIS-NIR) spectrum is very important. The corresponding results are shown in Fig. 7. While the VIS-NIR reflectance for a linearly graded film is in general lower than that of a quadratically graded film, the solar reflectance and hence the solar absorptance, a, of the 1 μm thick coating is close to that of the quadratically graded film. Considering the results of 0.5 μm thick films which yield different reflectance for linearly and quadratically graded profiles, it can be inferred that the solar absorptance can be varied by changing the grading profile and the thickness of coatings. This in turn allows a wide range of α/ϵ values. Thus, from the point of view of thermal control applications, it may be appropriate to use films having thicknesses less than 0.5 μm and a volume fraction of Ag, less than 0.20, in the entire coating.

In view of the potential applications of the films in many of the advanced systems wherein thermal stability of optical properties are very important, the optical properties of the films have been studied at different temperatures ranging from ambient to 120 ‘C. The results are presented in Figs. 8a and 8b. As can be seen, the optical properties are stable, exhibiting a deviation wit’hin 5% over a temperature change of 100 “C, which will have minimal effect on the functional performance of the coatings. The deviation is larger for thicker coatings which may be attributed to their higher metallic content.

5. Application to Tunnel IR Sensors

Linearly graded Ge:Ag films of thickness 0.5 μm have been applied to a novel micromachined uncooled electron tunneling infrared detector which primarily works on the principle of the Golay Cell but makes use of a highly sensitive tunneling current for measuring the expansion and hence the temperature of the micro gas cell[16]. The detector consists of a thin silicon rich silicon nitride membrane on which a thin film absorber coating is deposited. The desirable properties of the absorber coating are high infrared absorption, low thermal stress, low specific heat capacity, and high thermal conductivity. Previously a platinum coating of 2 nm thickness has been used as the infrared absorber. In this study the present composite graded films have been deposited on silicon-rich silicon nitride membranes for application to these devices. After detector assembly, detector performances were evaluated and compared with the earlier detectors. The Ge:Ag films have provided results on par with the best performance characteristics of the devices with the platinum films. It is important to add that there is further scope for improvement of the performance characteristics by varying the metal content, thickness, and grading profile. As is evident from the results presented in Figs 8a and 8b, these films can offer stable temperature performance by virtue of high degree of stability in optical properties against temperature variation. Furthermore, the deposition conditions for the films are very forgiving, allowing for wider process windows as opposed to the control of thin metal films on the nm scale -- a consideration for the mass production of the devices.

The present study of semiconductor-metal composite films and their applications is being extended to other composite systems such as Si:Au, the results of which will be presented elsewhere[17]. Such composite films offer scope for blending materials having diversified physical properties (optical, electrical, and magnetic) and to produce thin film devices which can have unique optical and thermal applications.

6. **Conclusions:**

Semiconductor:metal composite thin films offer an extensive scope for tailoring the optical properties in the infrared/visible optical spectrum for specific applications. Such tailoring is achieved by varying the coating thickness, concentration of metal and its grading profile. An example of this family, namely Germanium: Silver (Ge:Ag) composite thin films have been successfully prepared by simple dc magnetron sputtering and the optical properties have been studied. The investigation is being extended to the Si:Au system.

The experimental studies indicate that Ge in combination with various concentrations and profiles of Ag produce films having a wide range of controllable optical properties ranging from low reflectance/absorptance to high reflectance/absorptance which can be modeled. The spectral characteristics of the films against temperature are highly stable, making them extremely useful for many advanced applications in space and industrial systems. These films can have interesting applications such as selective infrared reflectors and high efficiency broad-band infrared absorbers.

The graded coatings have been successfully applied on micromachined uncooled infrared tunnel sensors (micro-Golay Cells). The coatings have shown excellent performance and offer wider scope for improvement over the current technology.

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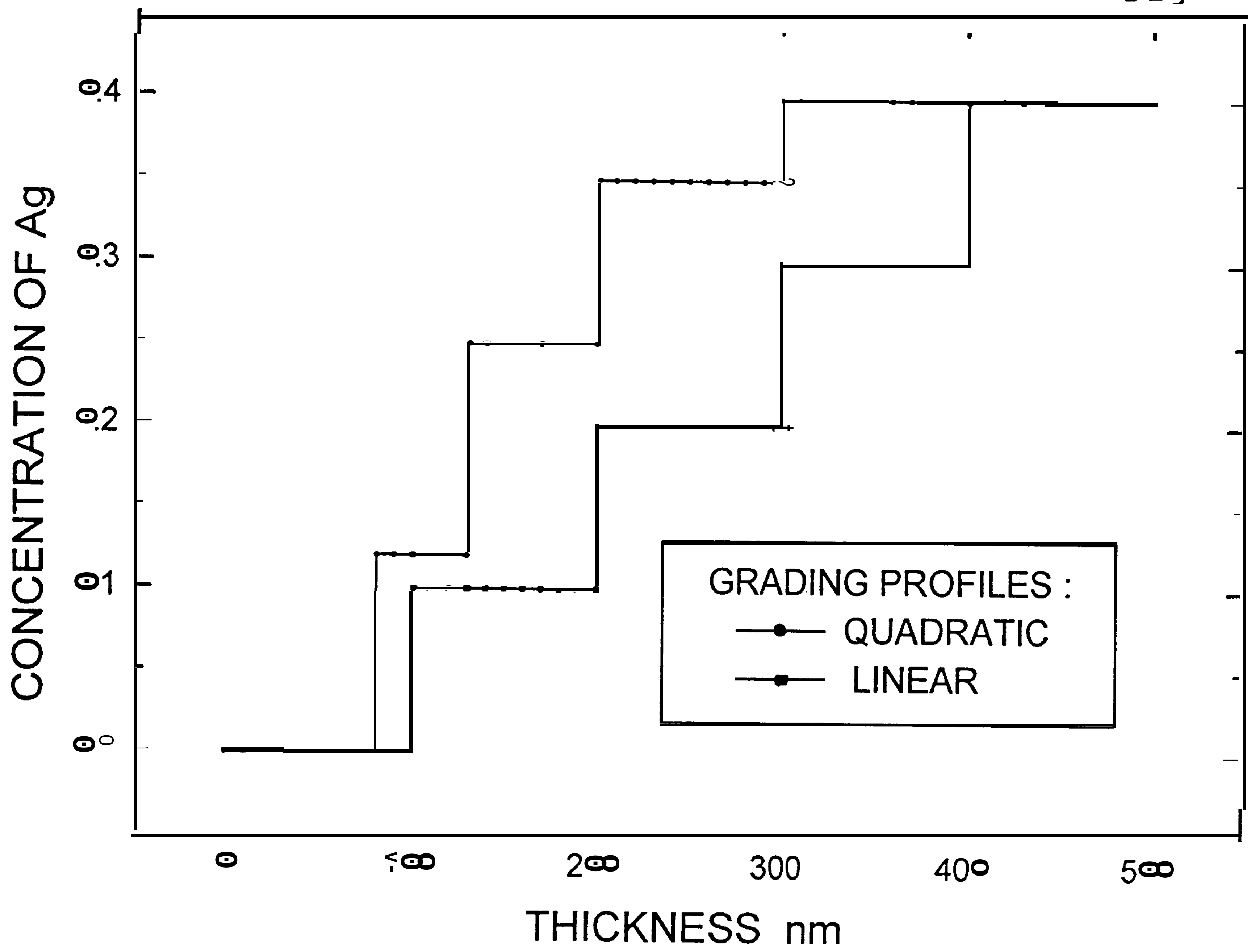
Fig. 1



CONCENTRATION OF Ag
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
THICKNESS nm
GRADING PROFILES :
QUADRATIC
LINEAR

Fig. 2

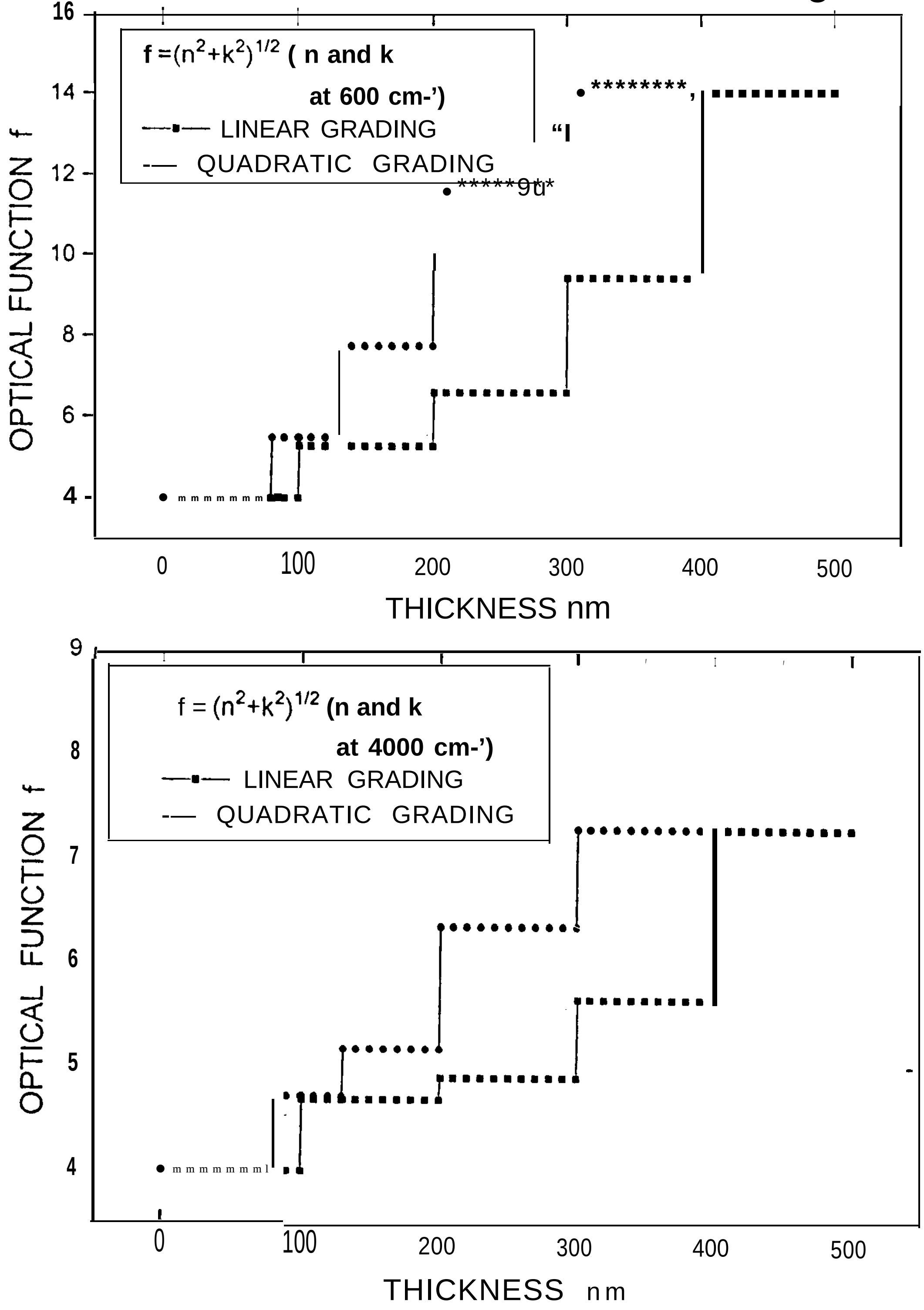

f =(n2+k2)1/2 (n and k
at 600 cm-')
LINEAR GRADING
QUADRATIC GRADING
OPTICAL FUNCTION f
16
14
12
10
8
6
4
0
100
200
300
400
500
THICKNESS nm
f = (n2+k2)1/2 (n and k
at 4000 cm-')
LINEAR GRADING
QUADRATIC GRADING
OPTICAL FUNCTION f
9
8
7
6
5
4
0
100
200
300
400
500
THICKNESS nm

Fig.3a

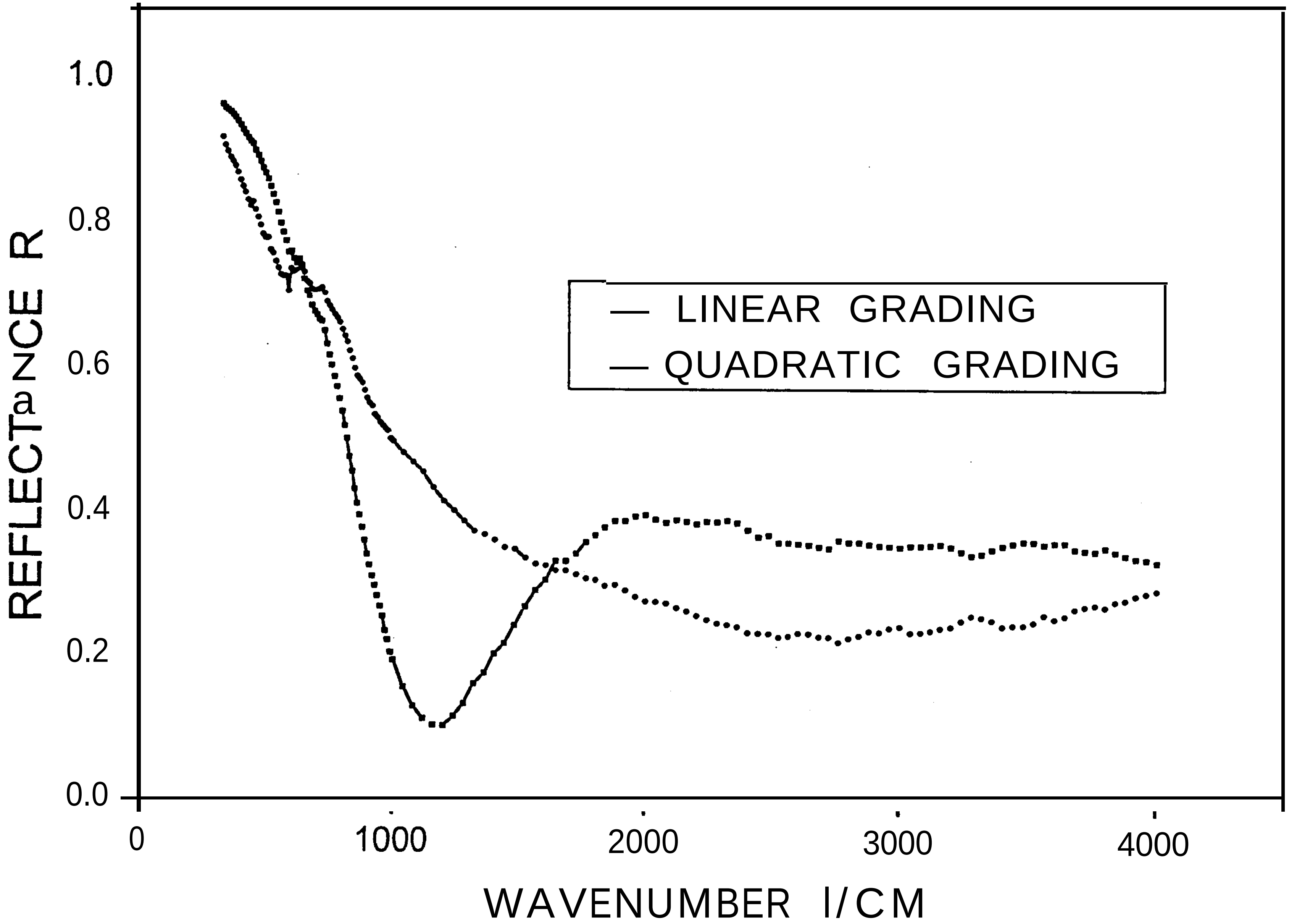

1.0
0.8
0.6
0.4
0.2
0.0
REFLECTaNCE R
— LINEAR GRADING
— QUADRATIC GRADING
0
1000
2000
3000
4000
WAVENUMBER l/CM

Fig 3b

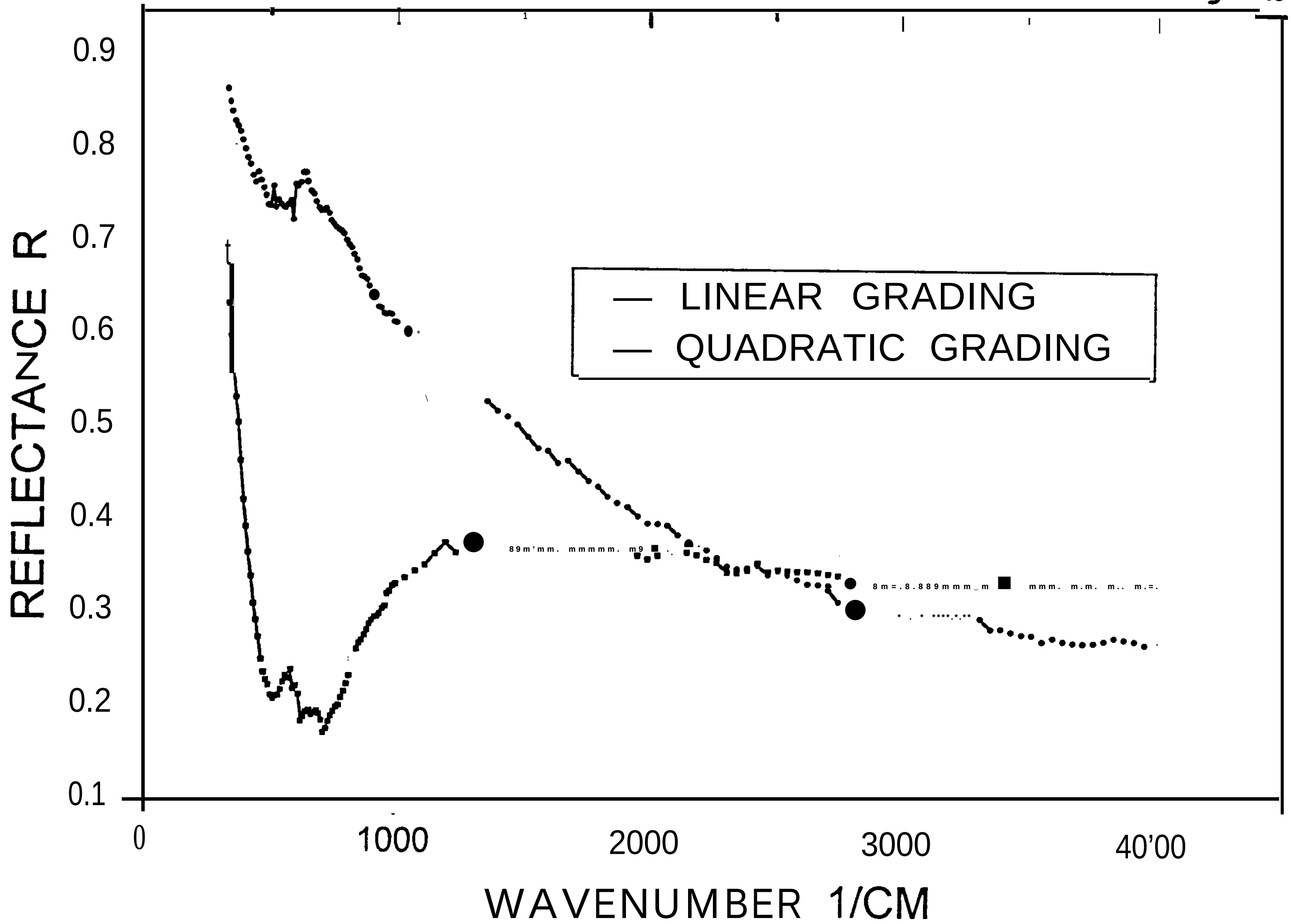
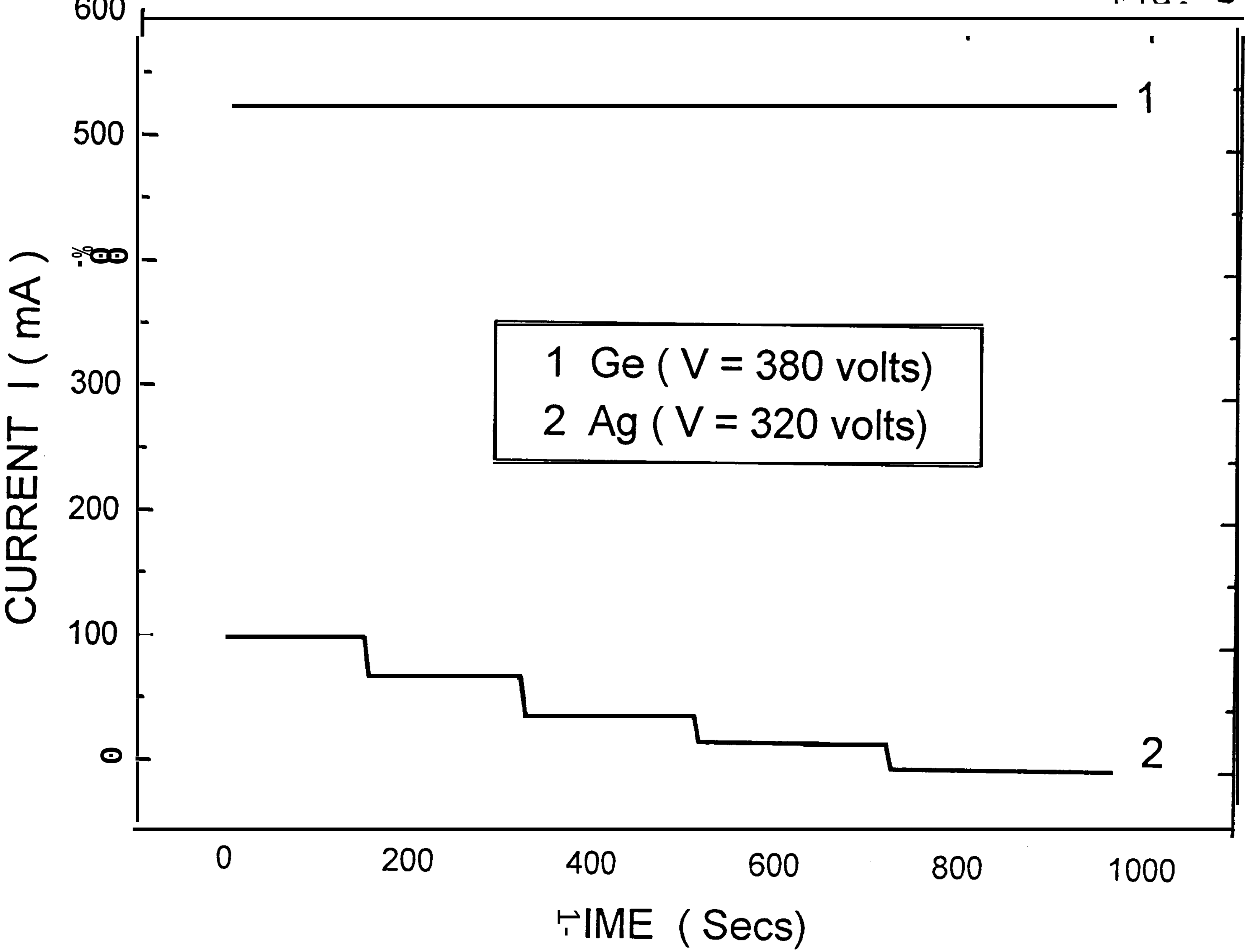
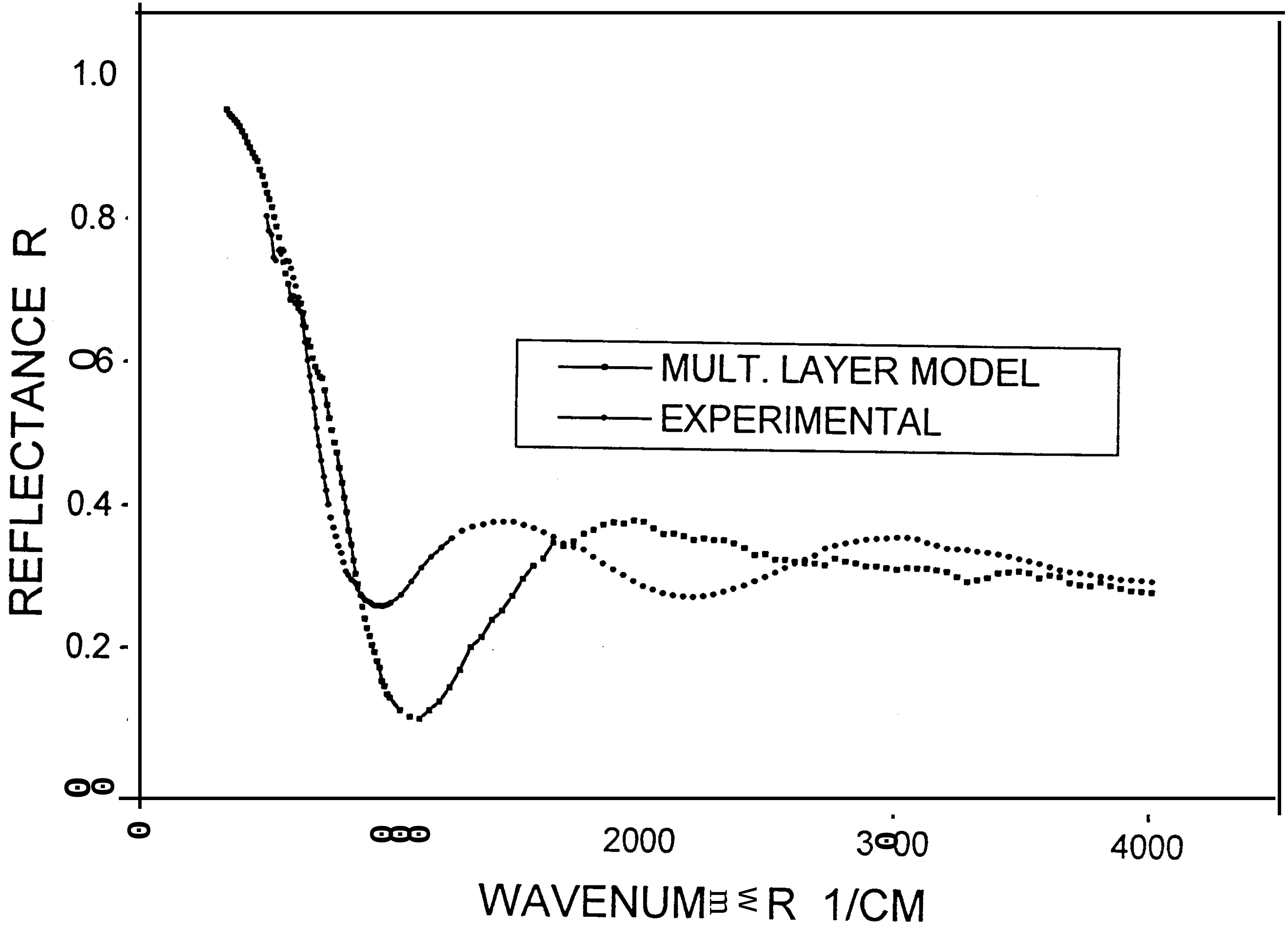

REFLECTANCE R
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
LINEAR GRADING
QUADRATIC GRADING
0
1000
2000
3000
40'00
WAVENUMBER 1/CM

Fig. 4



600
500
300
200
100
0
CURRENT I (mA)
1
2
1 Ge (V = 380 volts)
2 Ag (V = 320 volts)
0
200
400
600
800
1000
TIME (Secs)

Fig.5a



MULT. LAYER MODEL
EXPERIMENTAL
REFLECTANCE R
1.0
0.8
0.4
0.2
0
2000
4000
WAVENUMBER 1/CM

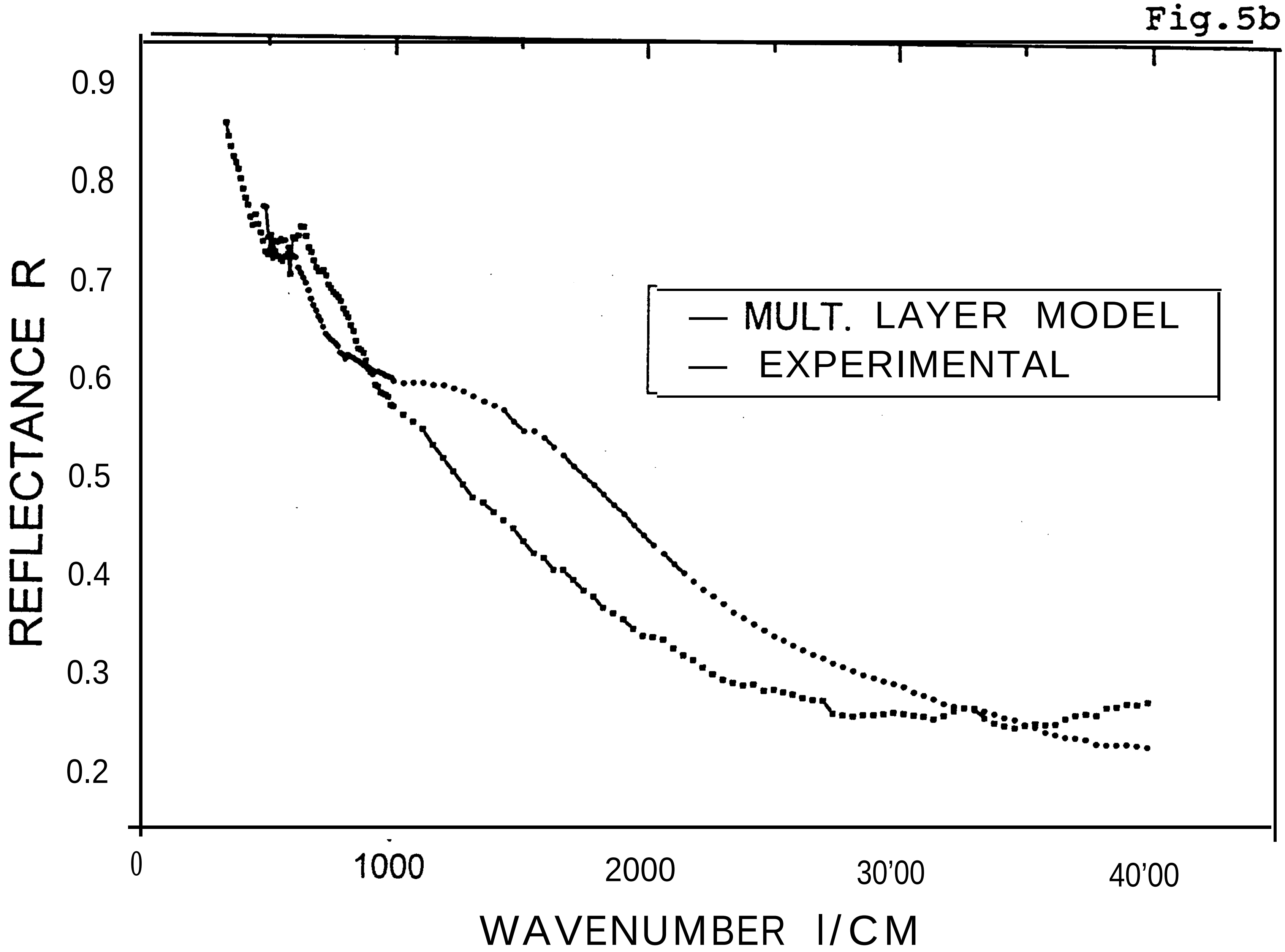
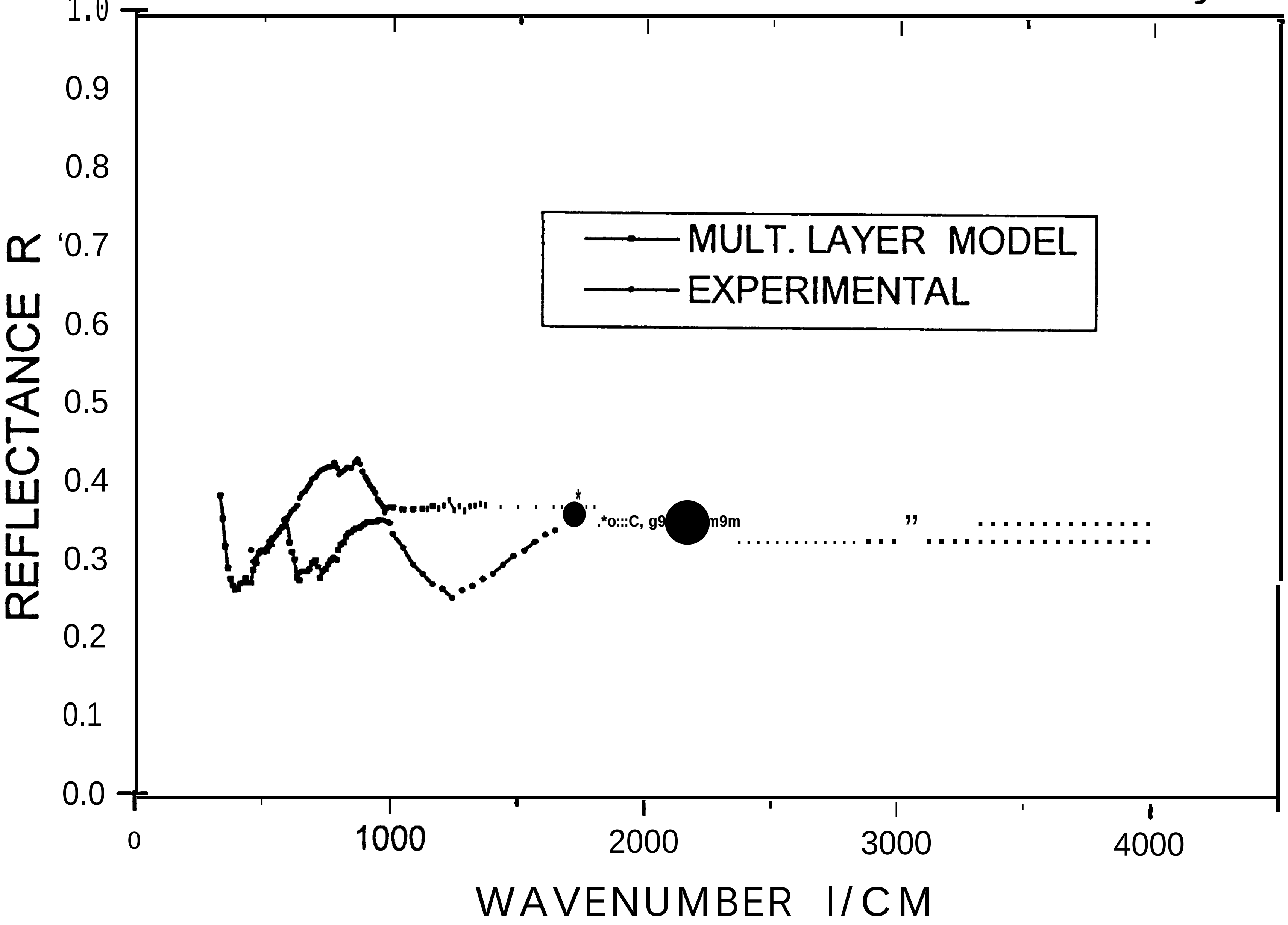


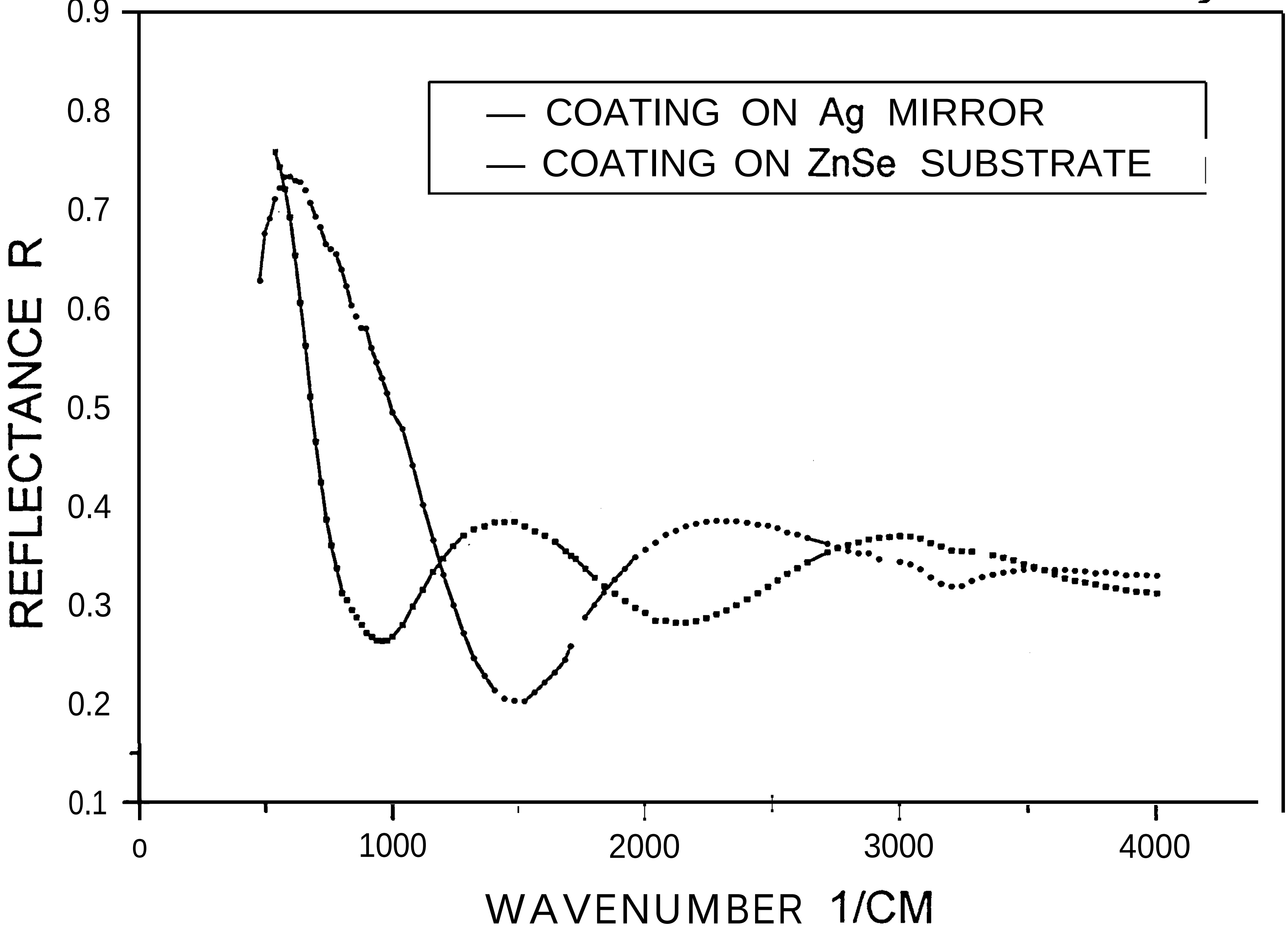
Fig.5b
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
REFLECTANCE R
— MULT. LAYER MODEL
— EXPERIMENTAL
0
1000
2000
30'00
40'00
WAVENUMBER l/CM

Fig.5c



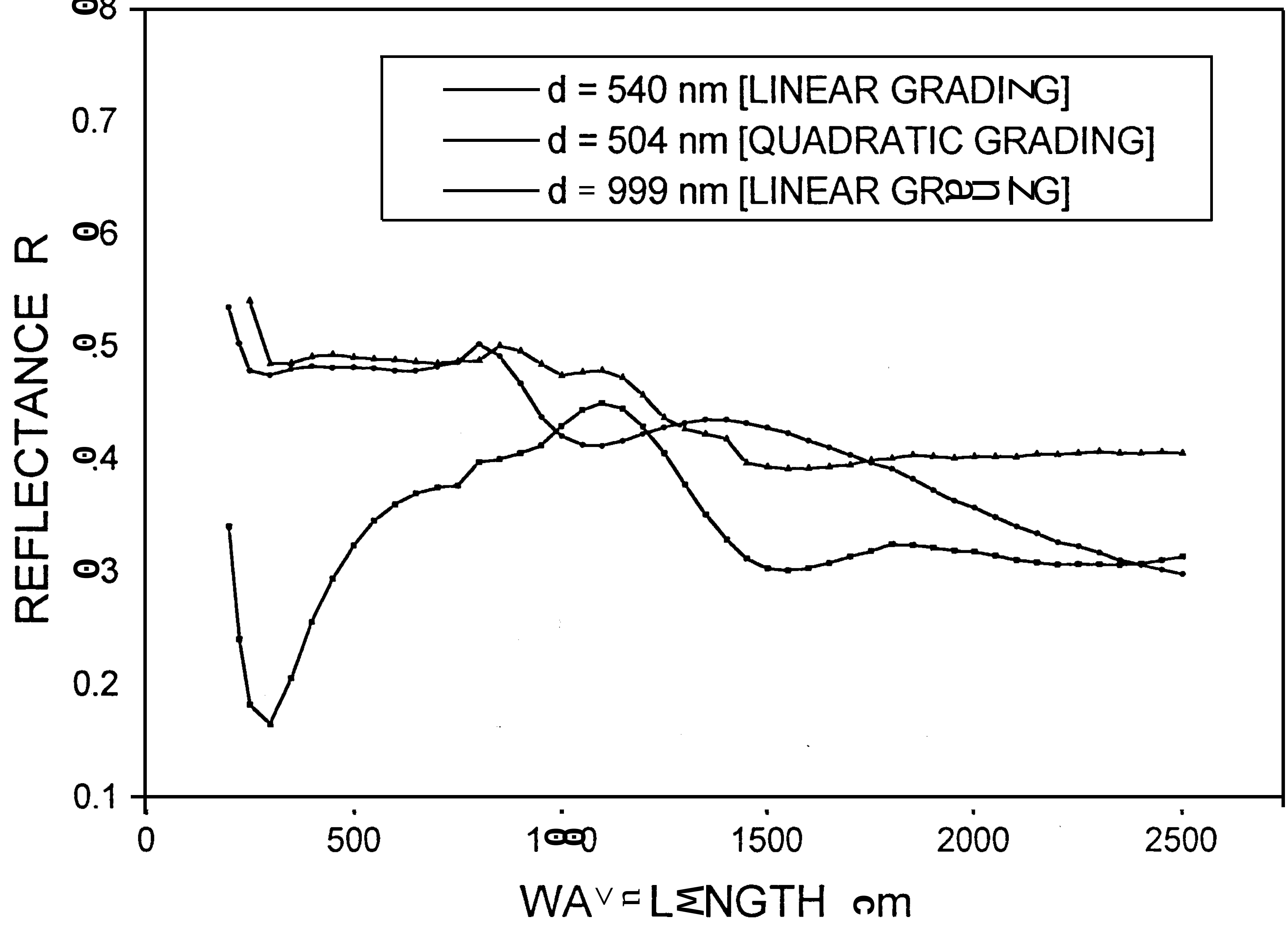
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
REFLECTANCE R
MULT. LAYER MODEL
EXPERIMENTAL
0
1000
2000
3000
4000
WAVENUMBER l/CM

Fig.6



— COATING ON Ag MIRROR
— COATING ON ZnSe SUBSTRATE
REFLECTANCE R
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1000
2000
3000
4000
WAVENUMBER 1/CM

Fig.7



d = 540 nm [LINEAR GRADING]
d = 504 nm [QUADRATIC GRADING]
d = 999 nm [LINEAR GRADING]
REFLECTANCE R
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
500
1000
1500
2000
2500
WAVELENGTH nm

Fig.8a

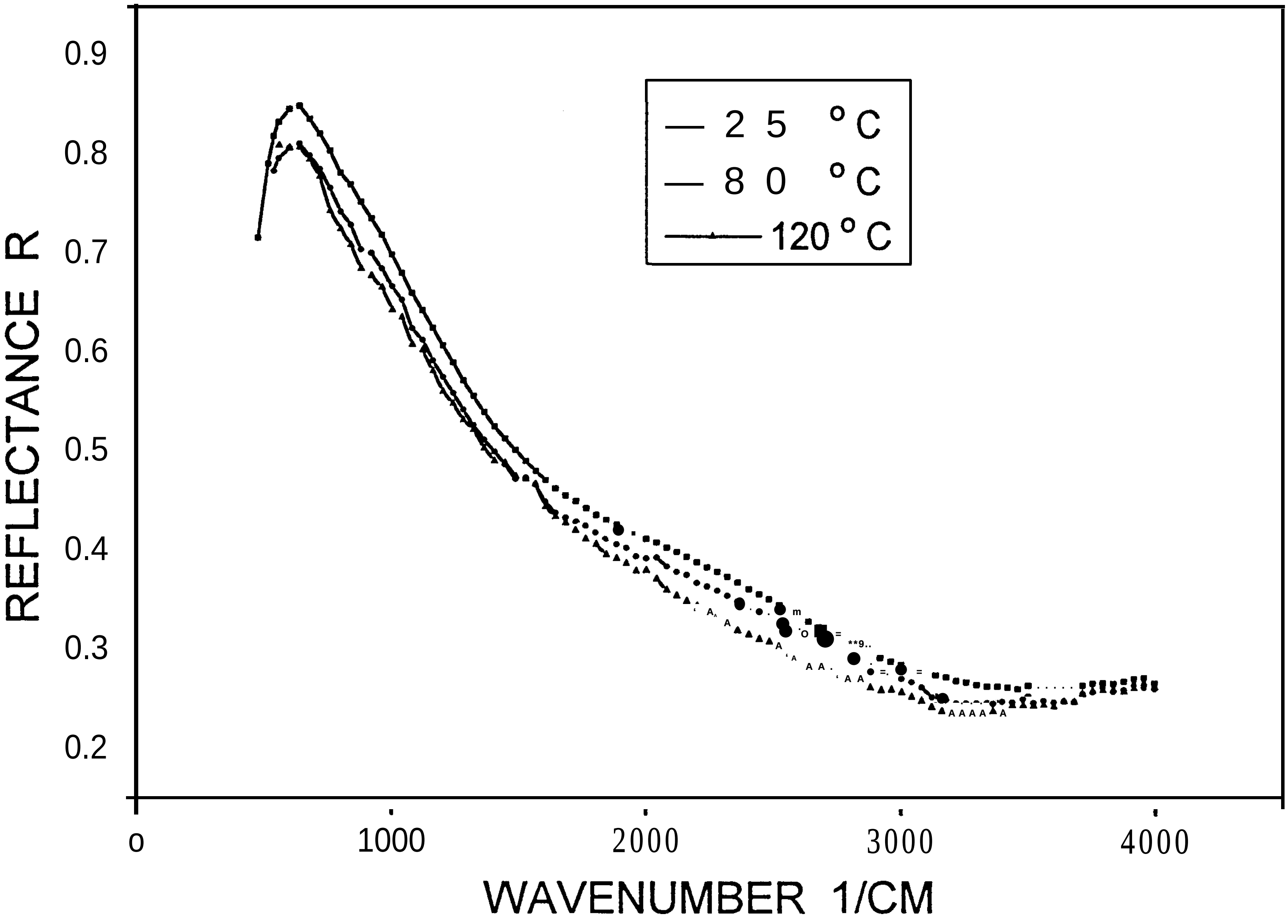
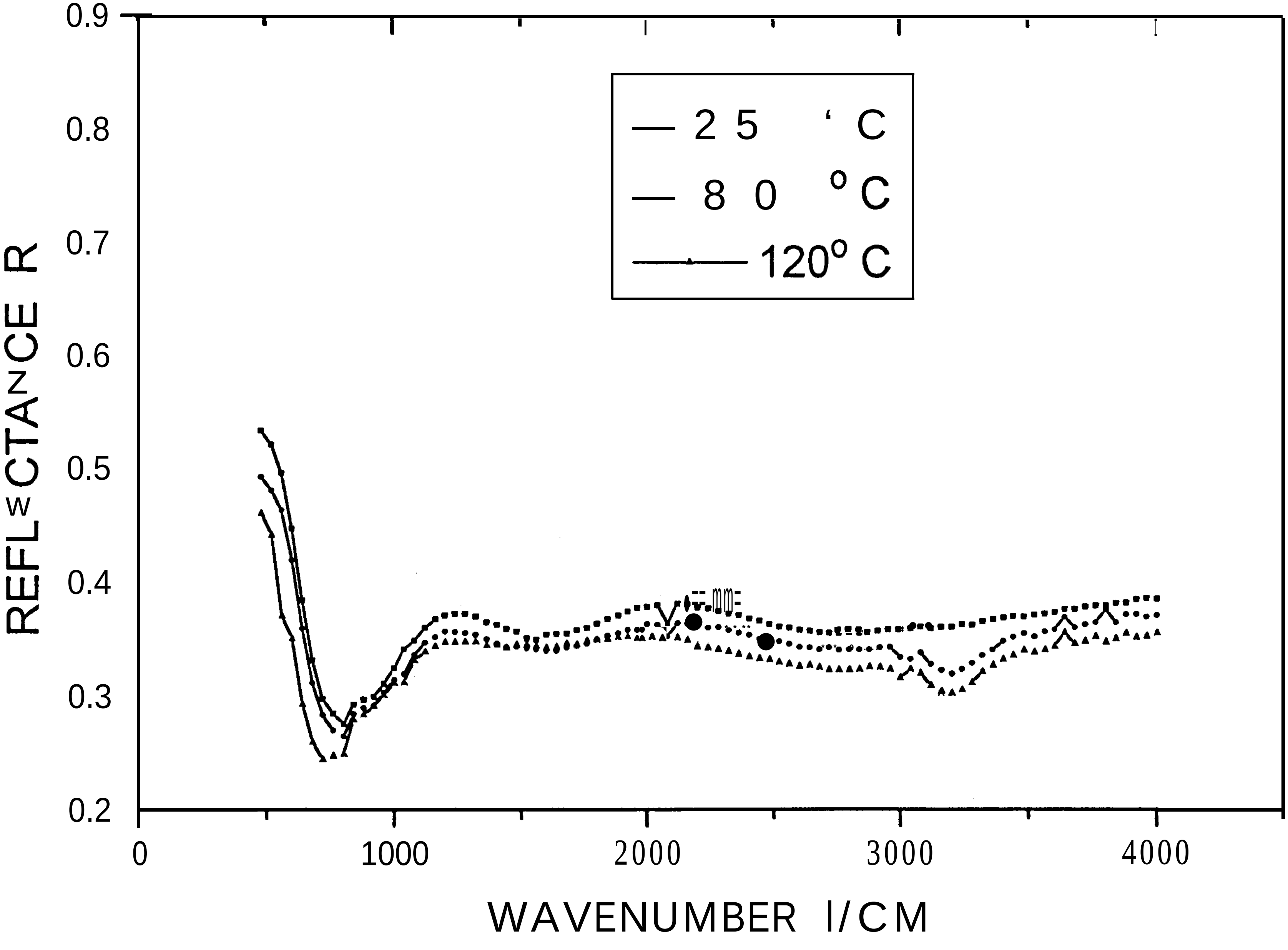

25 °C
80 °C
120 °C
REFLECTANCE R
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
1000
2000
3000
4000
WAVENUMBER 1/CM

Fig.8b



0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
REFLECTANCE R
25 °C
80 °C
120° C
0
1000
2000
3000
4000
WAVENUMBER l/CM

Figure Captions

Fig. 1 : Discontinuous metallic concentration profiles with respect to coating thickness, approximating continuous linear and quadratic profile forms.

Fig. 2 : Optical function variation with respect to coating thickness for discontinuous metallic concentration profiles.

Fig. 3 : Reflectance characteristics for graded Ge:Ag composite coatings 3a) 0.5μm thickness 3b) 1.0 μm thickness.

Fig. 4 : Input power characteristics for deposition of a 0.5 μm linearly graded Ge:Ag composite coating.

Fig.5a : Experimental spectral results of a 0.5 μm linearly graded Ge:Ag composite thin film on a Ag mirror coating and comparison with theory.

Fig.5b : Experimental spectral results of a 0.5 μm quadratically graded Ge:Ag composite thin film on a Ag mirror coating and comparison with theory.

Fig. 5c : Experimental spectral results of a 1.0 μm linearly graded Ge:Ag composite thin film on Ag mirror coating and comparison with theory.

Fig. 6 : Reflectance spectra of graded Ge:Ag composite films coated on a Ag mirror and a ZnSe substrate.

Fig.7 : Spectral reflectance of the graded Ge:Ag composite films on ZnSe in the VIS-NIR regions.

Fig. 8 : Reflectance of Ge:Ag graded composite films at higher temperatures, 8a) 0.5 μm and 8b) 1.0 μm,.